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Approaches to Bridged Planar Polypyridine, Polypyrazine, and Polythiophene Derivatives for
Maximization of Extended π -Conjugation.

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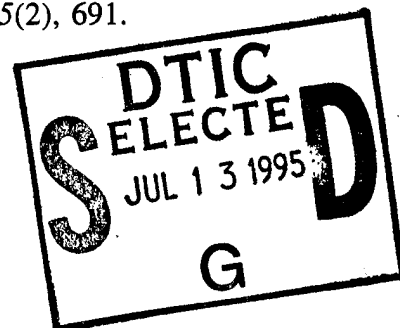
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Accepted for Publication in

Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **1994**, 35(2), 691.

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June 7, 1995



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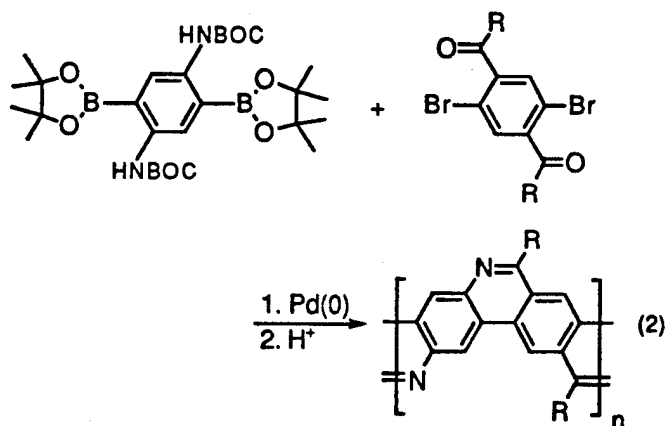
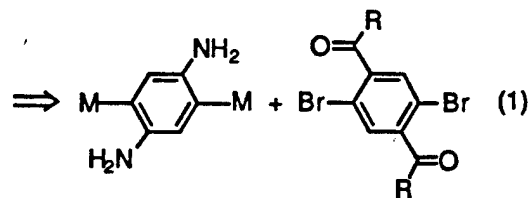
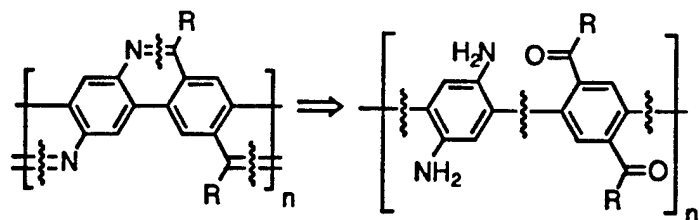
Approaches to Bridged Planar Polypyridine, Polypyrazine, and Polythiophene Derivatives for Maximization of Extended π -Conjugation

Yonghui Zhang, Qing Zhang, Jaydeep J. S. Lamba
and James M. Tour*

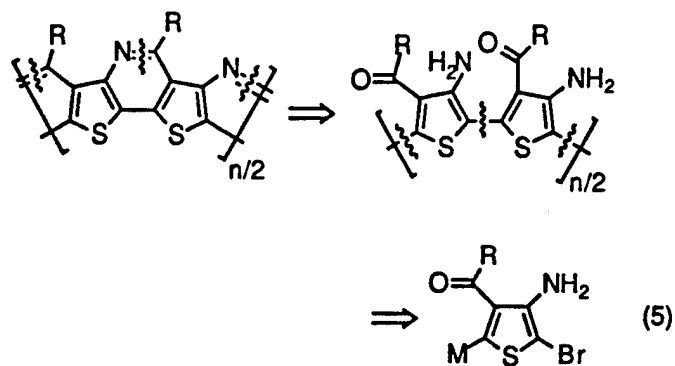
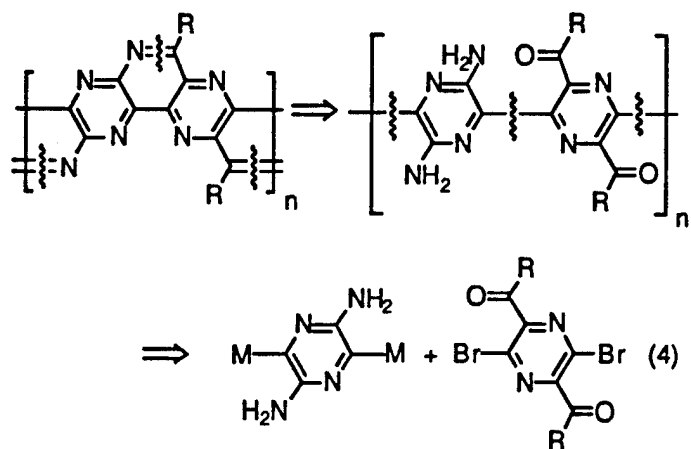
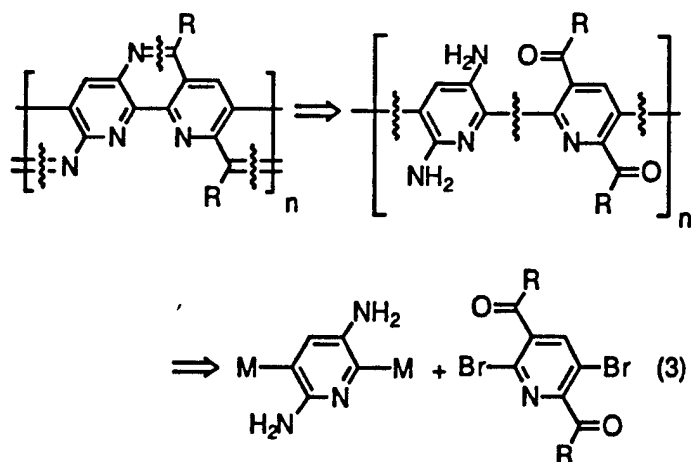
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We have been directing synthetic efforts toward the construction of conjugated macromolecules that are fixed in a planar conformation.¹ The planar conformations should maximize the extended π -conjugation. Additionally, the bridging units, if sp^2 -hybridized, should further increase the extended π -conjugation of the macromolecular systems.^{1,2} We previously described a synthetic route to planar poly(*p*-phenylene) derivatives by the retrosynthetic approach outlined in eq 1 (M = metal).³ The actual synthetic components are shown in eq 2.

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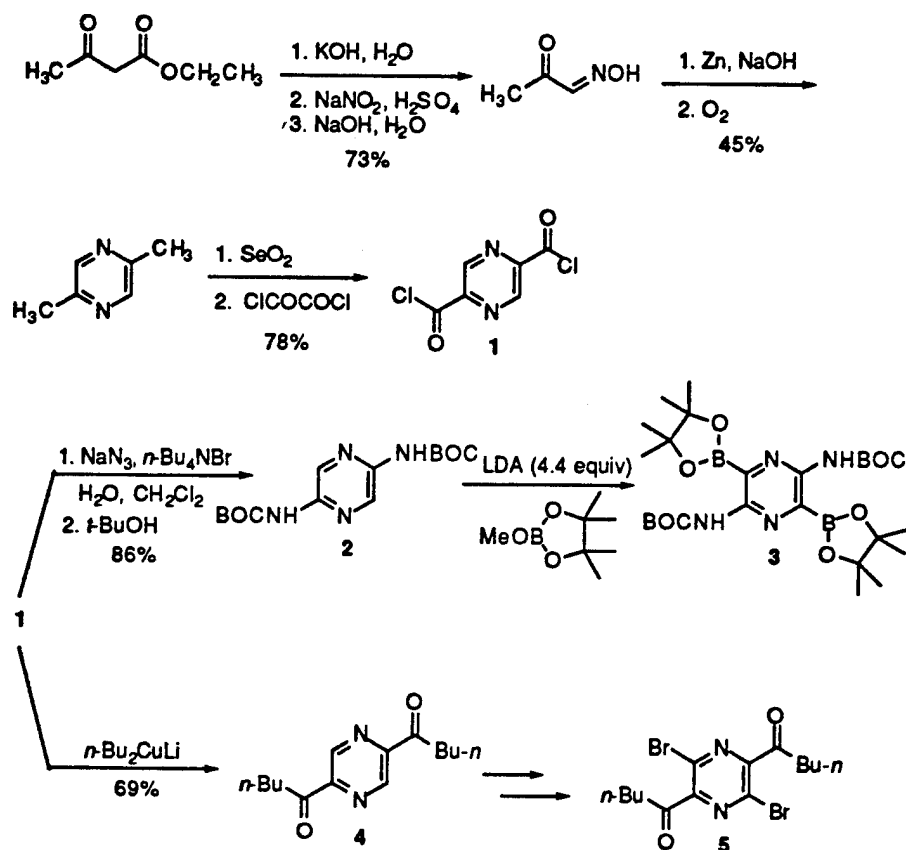


Here we describe our approach to the analogous planar polypyridine, polypyrazine, and polythiophene derivatives. The retrosynthetic approaches are shown in eqs 3-5, respectively (M = metal). The key features of these



retrosynthetic approaches are, first, imine cleavage to the ketone and amine functionalized polyaromatics, and second, bond cleavage to the AB-type polymerization monomers (eqs 1, 3, and 4) or the difunctional monomer (eq 5).

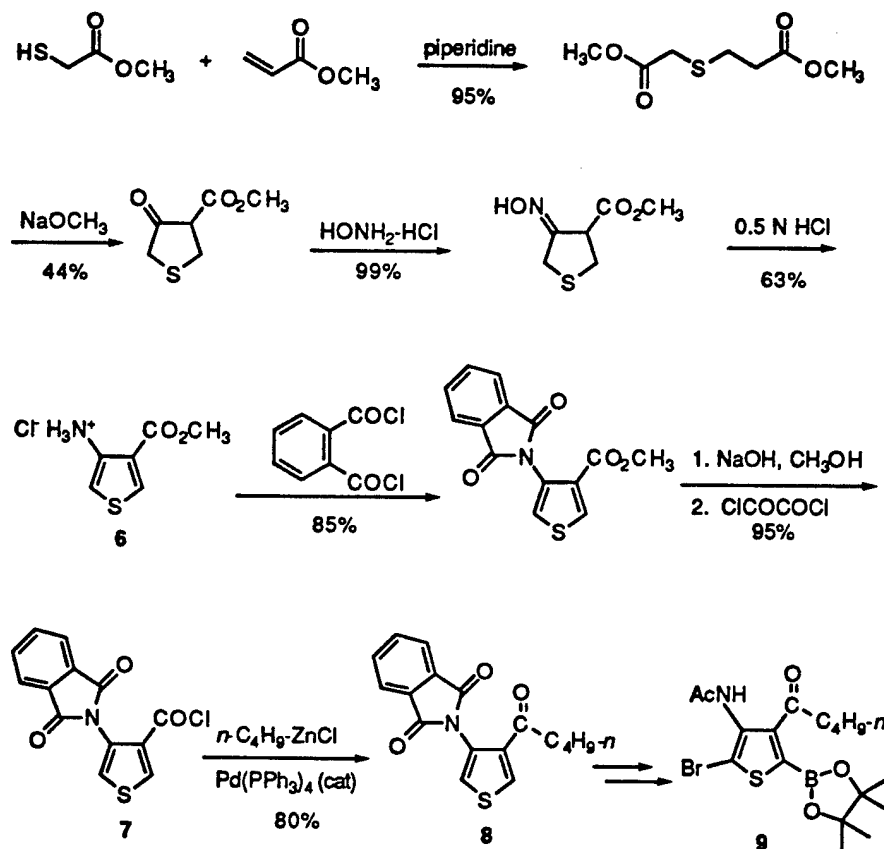
The desired monomers for the planar polypyrazine are being synthesized in the following manner. According to



standard protocol, ethyl acetoacetate was saponified, nitrosolated, and decarboxylated to form the α -ketooxime. Reduction and condensation afforded the dihydrodimethylpyrazine that was oxidized to dimethylpyrazine with air.⁴ Selenium dioxide-promoted diacid formation⁵ followed by treatment with oxalyl chloride afforded the pyrazine diacid chloride 1. This common intermediate could be used to synthesize both of the required monomers. First, conversion to the bis(acyl azide) under phase transfer conditions followed by a thermal bis-Curtius rearrangement and *t*-butanol capture afforded the bis(BOC)-protected diaminopyrazine 2.⁶ Remarkably, tetralithiation with LDA or LTMP followed by treatment with methyl pinacol borate afforded the required dimetalated diamine 3. The lithiation proceeded in very high yield since the tetralithio derivative could be quenched with TMSCl to afford the bis(trimethylsilyl)arene in 91% yield after aqueous work-up and purification. Further purification of the bis(boronic

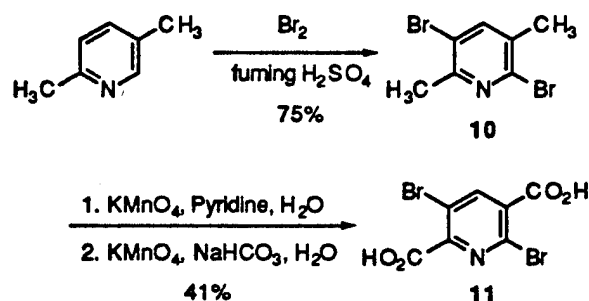
ester) is required. **1** could also be dibutylated with the dialkylcuprate to afford the required diketo functionality of the second monomeric intermediate (**4**). Methods for the selective bromination of **4** for the preparation of the required diketodibromide **5** are currently being developed. The superb efficiency of this divergent (common intermediate **1**) approach is indeed apparent.

The required monomer for the planar polythiophene is being prepared in the following manner. Standard protocol



was used for thiol conjugate addition, ester enolate formation, cyclization, oxime formation, and dehydration to afford the thiophene skeleton (**6**) with the amine and carbonyl moieties in place.⁷ Imide formation, saponification, and acid chloride formation afforded **7** which could be converted to the ketone (**8**) with butylzinc chloride and Pd(0) catalysis.⁸ We are presently working on methods to permit 2-position bromination and 5-position metalation to afford the required monomer **9** for the step growth polymerization.

Our approach to the planar polypyridine monomers is less well-developed, however, our progress is as outlined below. Dimethylpyridine was brominated under forcing



conditions to yield **10**.⁹ A two step oxidation procedure afforded the desired dibrombis(acid) **11**.¹⁰ We hope to utilize a divergent approach as outlined for **1** to convert **11** into the two monomers needed for the planar polypyridine material.

Acknowledgments. We are grateful for support from the Office of Naval Research, and the National Science Foundation (EHR-91-08772, DMR-9158315), and generous industrial contributors to the NSF Presidential Young Investigator Award (1991-96): Hercules, IBM, Ethyl, Shell, Exxon, Farchan, Molecular Design Ltd., and Eli Lilly Corporations.

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